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Combined Use of Pulsed Gradient Spin Echo and High Resolution Magic Angle Spinning to Investigate Solutes Diffusion in Presence of a Chromatographic Stationary Phase

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1. Introduction

We recently introduced a novel analytical method based on the Pulsed Gradient Spin Echo (PGSE) experiment and High Resolution Magic Angle Spinning (HRMAS), which combines the advantages of column chromatography separation and NMR structural analysis [1]. Specifically, we showed that, in a PGSE experiment, the separation of the NMR spectra of the components of a mixture could be enhanced by several orders of magnitude upon addition of a typical stationary phase used in HPLC, such as either a normal (silica gel) or a reversed (functionalized ODS silica gel) phase. HRMAS is then required to recover high resolution NMR spectra by removing magnetic susceptibility broadenings caused by the presence in solution of the solid support. This combined PGSE and HRMAS technique was subsequently applied to investigate indirectly crucial steps of reversed phase liquid chromatography, such as the partitioning of the analyte between different phases [2].

Interestingly, with respect to HPLC, this technique offers surprising perspectives for mixture analysis [3]. Indeed, while reversed phase liquid chromatography (RPLC) is required to separate the components of a model mixture (benzene, naphthalene, and anthracene dissolved in an acetonitrile/water mix), both normal and reversed stationary phases give excellent discrimination in NMR. Because of its unexpected potential for mixture analysis, this technique was hence referred to as 'Chromatographic NMR'.

To investigate the discrimination process evidenced in Chromatographic NMR, the apparent diffusion coefficients (D) of the above mentioned 3-component mixture were measured in the presence of a constant weight of bare silica as a function of the amount of liquid solution in the MAS rotor.

2. Results and Discussion

The discrimination obtained for benzene, naphthalene, and anthracene, in an acetonitrile/water mix, is best illustrated in the form of a DOSY map (Fig. 1). Basically, Diffusion Ordered NMR Spectroscopy (DOSY) is a convenient way of displaying PGSE data showing a pseudo two-dimensional spectrum with chemical shifts and D values on the horizontal and vertical axes, respectively [4]. In this way, the orders of magnitude difference in the diffusion coefficients of the three solutes is clearly apparent.

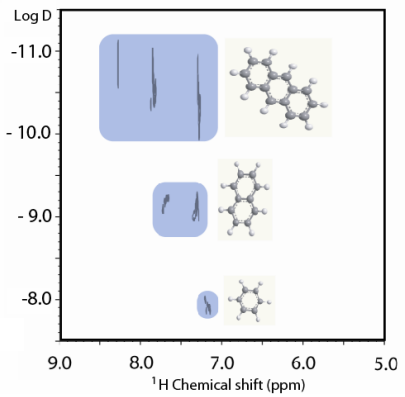

Fig. 1. DOSY map recorded at 303 K on a mixture of benzene, naphthalene, and anthracene, at 90.0, 9.0, and 1.6 g L^{-1}, respectively, in an acetonitrile/water mix (90/10, v/v).

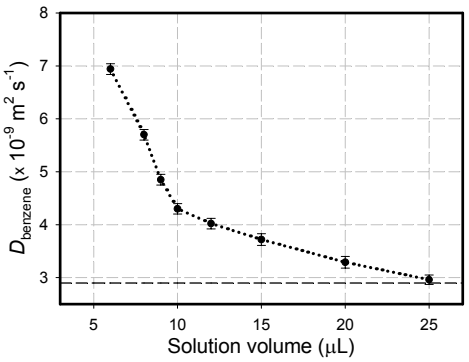

Fig. 2. Diffusion coefficient of benzene in $CDCl_3$ (1 g L^{-1}) at 303 K with the bare silica. The dashed line shows the diffusion coefficient of benzene measured in the same conditions without stationary phase.

Initially, this particular system was selected as a model because it is commonly employed in RPLC for testing the properties of the chromatographic support used under reversed phase conditions. However, due to differences in solubility, the solutes concentrations are very different. Therefore, another solvent was required and $CDCl_3$ was first tried because it is a good solvent for aromatics and compatible with bare silica. Surprisingly, a clear discrimination could also be observed in this case.

Subsequently, the *D* values of the three components analyzed separately in $CDCl_3$ were measured as a function of the solution volume. While relatively little variation was observed for both naphthalene and anthracene, the *D* value of benzene clearly increased as the solution amount was reduced (Fig. 2). This may be related to the work of D'Orazio *et al.* [5] who described a vapor phase contribution to the diffusion of water confined in porous glass with different filling fractions. As a consequence of this specific molecular behavior, the differences in *D* can be modulated.

3. Conclusion

These preliminary results show that, in loose analogy to HPLC, several physicochemical parameters can be fruitfully used to optimize the resolution in Chromatographic NMR.

References

[1] S. Viel, F. Ziarelli, S. Caldarelli, Proc. Natl. Aca. Sci. USA 100 (2003) 9696-9698.
[2] G. Pagès, C. Delaurent, S. Caldarelli, Anal. Chem. 78 (2006) 561-566.
[3] G. Pagès, C. Delaurent, S. Caldarelli, Angew. Chem. Int. Ed. 45 (2006) 5950-5953.
[4] K. F. Morris, C. S. Johnson, Jr. J. Am. Chem. Soc. 114 (1992) 3139-3141.
[5] F. D'Orazio, S. Bhattacharja, W. P. Halperin, R. Gerhardt Phys. Rev. Lett. 63 (1989) 43-46.